AD-A234 596

SECURITY CLAS

REPORT DOCUMENTATION PAGE

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1a. REPORT SECURITY CLASSIFICATION	1b. RESTRICTIVE MARKINGS
Unclassified	

2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION / AVAILABILITY OF REPORT
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE	

4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
Technical Report No. 30	

6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
The University of Texas at Arlington		Office of Naval Research

6c. ADDRESS (City, State, and ZIP Code)	7b. ADDRESS (City, State, and ZIP Code)
Center for Advanced Polymer Research Department of Chemistry, Box 19065, University of Texas at Arlington, Arlington, TX. 76019	800 North Quincy Street Arlington, Virginia 22217

8a. NAME OF FUNDING / SPONSORING ORGANIZATION Defense Advanced Research Projects Agency	8b. OFFICE SYMBOL (If applicable) DARPA	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-90-J-1320

8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS			
1410 Wilson Boulevard Arlington, Virginia 22209	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION N

11. TITLE (Include Security Classification)

Processable Polymers and Copolymers of 3-Alkylthiophenes and Their Blends

12. PERSONAL AUTHOR(S) Martin Pomerantz, John J. Tseng, Hong Zhu, Steven J. Sproull, John R. Reynolds, Robert Uitz, Howard J. Arnott and M. Ishaq Haider

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Technical	FROM _____ TO _____	April 12, 1991	7

16. SUPPLEMENTARY NOTATION

Paper in press in Synthetic Metals, presented at the International Conference on Science and Technology of Synthetic Metals, Tubingen, West Germany, September 1990

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Poly(3-alkylthiophenes); molecular weight; copolymers; blends; fibers; films

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

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20. DISTRIBUTION / AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☑ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL
Dr. JoAnn Milliken	(202) 696-4410	

DD FORM 1473, 84 MAR   83 APR edition may be used until exhausted.   SECURITY CLASSIFICATION OF THIS PAGE
All other editions are obsolete.

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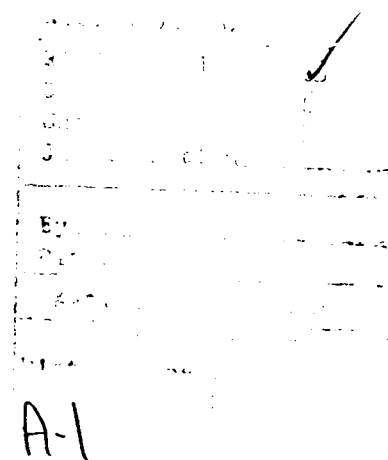DEFENSE ADVANCED RESEARCH PROJECTS AGENCY/OFFICE OF NAVAL RESEARCH

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by

Martin Pomerantz
John J. Tseng
Hong Zhu
Steven J. Sproull
John R. Reynolds
Robert Uitz
Howard J. Arnott
M. Ishaq Haider

Center for Advanced Polymer Research
Department of Chemistry
Box 19065
The University of Texas at Arlington
Arlington, Texas 76019-0065

April 12, 1991

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PROCESSABLE POLYMERS AND COPOLYMERS OF 3-ALKYLTHIOPHENES AND THEIR BLENDS

MARTIN POMERANTZ,*‡ JOHN J. TSENG,‡ HONG ZHU,‡ STEVEN J. SPROULL,‡ JOHN R. REYNOLDS,*‡ ROBERT UITZ‡ and HOWARD J. ARNOTT†

‡Center for Advanced Polymer Research. Department of Chemistry and †Department of Biology, The University of Texas at Arlington. Arlington, TX 76019-0065 (U.S.A.)

M. ISHAQ HAIDER

Research Division, Hoechst-Celanese Corporation, Summit, NJ 07091 (U.S.A.)

ABSTRACT

Poly(3-alkylthiophenes) have been prepared using anhydrous $FeCl_3$ in $CHCl_3$ while dry air was bubbled through the reaction mixture. Molecular weight studies via GPC, using polystyrene standards in conjunction with RI and UV detection along with absolute determinations using a multiangle laser light scattering (MALLS) detector, have shown these materials are of high molecular weight (M_w of up to 400,000) and relatively low polydispersity ($M_w/M_n < 3$). Further, the MALLS detector (absolute molecular weights) provides weight average molecular weights 2-5 times larger than those obtained using polystyrene standards showing that polystyrene is a rather poor standard for these materials. A series of copolymers of the 3-alkylthiophenes was prepared using a 1:1 molar feed ratio of the two monomers and the molecular weights of the materials decreased with decreasing side chain length. Poly(3-alkylthiophenes) were processable via a variety of methods, including melt spinning to form soft fibers. The films and fibers were dopable with typical oxidants to conductivities of up to 5 Ω^{-1} cm^{-1}. The solution pulled fibers were observed to be birefringent with considerable orientation along the fiber axis. EDAX studies have shown that the doping of melt-spun fibers was quite uniform. Blends of poly(3-decylthiophene) with low density polyethylene have been prepared and melt-spun into fibers. Blends prepared by melt-blending the components were seen by electron microscopy to be phase separated into large domains while those prepared from xylene solution were much more uniform. Spinning was easier with the blends and the fibers spun from the blend prepared from xylene solution was seen to be birefringent with considerable orientation along the fiber axis. Doping of the melt spun fibers obtained from xylene solution formed blends gave conductivities of ca. $10^{-1} - 1$ Ω^{-1} cm^{-1} while those produced from the melt formed blends were non-conducting.

INTRODUCTION

In recent years there has been enormous interest in the area of electronically conducting polymers which display a wide range of electrical conductivities. Polythiophene, which is a prototypical highly conjugated polymer which becomes electronically conducting upon doping is, unfortunately, intractable. It has been found that substitution at the 3-position of the thiophene ring with, for example, an alkyl chain of 4 or more carbon atoms, renders the polymers soluble in many

organic solvents in both the undoped and doped states.[1-7] In addition, the longer chain poly(3-alkylthiophenes) show readily accessible "melting" (softening) points and can be melt processed.[1,3b,5,8] A convenient chemical method for the preparation of these polymers, first employed by Yoshino and coworkers using transition metal halides such as $FeCl_3$, $MoCl_5$ and $RuCl_3$,[9] involves Lewis acid promoted polymerization of the 3-alkylthiophene monomers, generally using $FeCl_3$ (equation 1).[5,6,10-12]

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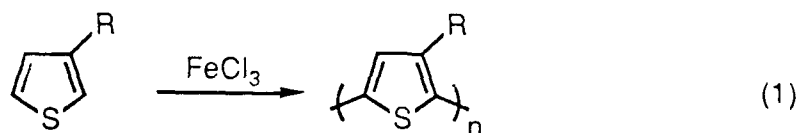
Molecular weights of some of the poly(3-alkylthiophenes) have been reported and it appears that those polymers prepared by $FeCl_3$ oxidative polymerization have higher molecular weights than those prepared electrochemically or by chemical coupling of halogenated derivatives. Weight average molecular weights (GPC relative to polystyrene standards) of up to about 250,000 have been reported, but generally the polydispersity has been quite large.[5,6,10]

In this paper we report on the preparation of high molecular weight poly(3-alkylthiophenes) of fairly narrow polydispersity, and on the study of the molecular weights of these homopolymers and several copolymers by GPC. These GPC studies were done both relative to polystyrene standards and by absolute measurements using a multiangle laser light scattering GPC detector. We also report on studies of melt-spun fibers of the pure polymers and of blends with low density polyethylene. The former have been oxidatively doped with $FeCl_3$ to conductivities as high as 5 Ω^{-1} cm^{-1}.

EXPERIMENTAL SECTION

General. GPC was done on a Waters GPC-II instrument with Ultrastyrogel columns (10,000, 500, and 100 Å) with an RI, a UV-VIS and a Wyatt Technology multiangle laser light scattering detector in series and, for the RI and UV-VIS detectors, polystyrene standards. Electron microscopy was performed on a JEOL-35 C SEM instrument and optical microscopy on a Leitz Laborlux microscope. Bulk poly(3-decylthiophene) or blends were formed into rods (0.5 in. dia. by 2.5 in. long) which were melt spun at ca. 180-300 °C into monofilaments at various spinning speeds. Films were prepared by solution casting of carefully filtered trichloroethylene polymer solutions on glass. These films could be oriented by hand stretching to l/l_o = 1.5.

3-Alkylthiophenes. Monomers were prepared by coupling of the alkylmagnesium bromide with bromothiophene in the presence of Ni(dppp)Br$_2$ according to the method of Kumada, et al.[7]

Poly(3-alkylthiophenes). Into a 100 mL 3-necked flask equipped with a magnetic stirring bar, condenser, dropping funnel and an inlet for dry air was put 7 mmol of the 3-alkylthiophene. A solution of 1.0 g of anhydrous $FeCl_3$ in 50 mL of chloroform was added to the alkylthiophene over about 20 min. and the solution became dark. The mixture was then warmed to 50 °C and stirred for 24 h at this temperature, while dry air was bubbled through. The black mixture was washed with water to remove excess $FeCl_3$ to give a dark green-black mixture. This was stirred with 20 mL of conc. aqueous ammonia and chloroform for 30 min. at room temperature to produce a yellowish-red chloroform solution which was washed several times with water and dried over $MgSO_4$. Removal of the solvent gave a 60-97% yield of the dark purple poly(3-alkylthiophene). Soxhlet extraction with methanol was used to remove the low molecular weight fractions from the bulk polymer.

Oxidative Doping. Doping of the films and fibers was carried out using $FeCl_3$ or $Fe(ClO_4)_3$

solutions of varying concentrations in CH_3CN or CH_3NO_2 at room temperature.

RESULTS AND DISCUSSION

Our syntheses of poly(3-alkylthiophenes) involve polymerization of the monomer with anhydrous $FeCl_3$ in $CHCl_3$ while bubbling dry air through the reaction mixture. After dedoping with conc. ammonia the low molecular weight species were removed by methanol extraction. The polymers which we have prepared are poly(3-butylthiophene) (**1**), poly(3-hexylthiophene) (**2**), poly(3-octylthiophene) (**3**), poly(3-decylthiophene) (**4**) and poly(3-dodecylthiophene) (**5**) and all had the appropriate ^1H and ^{13}C NMR spectra and IR spectra and appeared quite similar to the reported polymers prepared without air. However, the use of air gave material of somewhat higher molecular weight. In the case of poly(3-butylthiophene) (**1**) there was a small band at 1713 cm^{-1} which was probably a small carbonyl impurity. The UV-VIS spectra were all quite similar with maxima ($CHCl_3$ solution) between 420 and 440 nm indicating all had similarly high molecular weights. Further, as expected, they all exhibited solvatochromism with, for example, λ_{max} for **4** going from 440 nm in $CHCl_3$ to 490 nm as a solid film.

Molecular weights were obtained by gel permeation chromatography (GPC) two different ways. The first was by comparison with polystyrene standards using both refractive index (RI) and ultraviolet-visible (UV-VIS) detectors. In the second absolute molecular weights were obtained using a multiangle laser light scattering (MALLS) detector in conjunction with the RI detector. All three detectors were put in series and thus all measurements were made on the same sample at the same time. In addition, dn/dc (the change in refractive index with concentration) was determined for each of the polymers. The results are presented in Table 1. What can be seen is that all samples are of high

TABLE 1. Poly(3-alkylthiophenes) GPC Molecular Weight Determination (Polystyrene Standards vs. Absolute)

R	RI Detector M_w	UV Detector (254nm) M_w	Multiangle Laser Light Scattering Detector (MALLS)			
			M_w	M_n	Peak Max.	M_w/M_n
C_4H_9 (**1**)	68,000	126,000	340,000	205,000	280,000	1.7
C_6H_{13} (**2**)	175,000	124,000	398,000	297,000	320,000	1.3
C_8H_{17} (**3**)	98,000	77,000	204,000	136,000	190,000	1.5
$C_{10}H_{21}$ (**4**)	127,000	146,000	390,000	187,000	260,000	2.1
$C_{12}H_{25}$ (**5**)	121,000	107,000	227,000	99,000	88,000	2.5

molecular weight and in all cases the molecular weights (M_w) obtained by the MALLS detector, which provides absolute molecular weights, are larger by factors of up to 5 relative to those obtained with polystyrene standards using either an RI or UV-VIS (254 nm) detector. Also in the table is the absolute molecular weight at the maximum of the concentration distribution (determined by the RI detector). Thus it is clear that polystyrene is a rather poor standard for the determination of the molecular weights of poly(3-alkylthiophenes).

In order to examine the preparation reproduciblity, five identical reactions were run to give **3** (Table 2). As can be seen, the molecular weights were quite high but varied somewhat indicating the preparation was not totally reproducible. Again, the MALLS detector provided molecular weights

TABLE 2. Poly(3-octylthiophene) GPC Molecular Weights
(Polystyrene Standards vs. Absolute)

Sample	RI Detector	UV Detector (254nm)	Multiangle Laser Light Scattering Detector (MALLS)			
	M_w	M_w	M_w	M_n	Peak Max.	M_w/M_n
1	61,000	85,800	112,600	62,000	81,900	1.8
2	69,800	92,100	212,500	118,700	116,600	1.8
3	68,700	95,400	244,700	118,700	147,400	2.1
4	35,700	54,700	164,100	100,800	138,300	1.6
5	95,400	121,900	306,500	112,600	191,200	2.7

considerably larger than those obtained using polystyrene standards.

Several copolymers were prepared by polymerizing equal molar amounts of the two monomers with $FeCl_3$/air. (No attempt was made to determine the exact ratio of the two monomers in the polymer.) The results are presented in Table 3. What can be seen, is that, in addition to the MALLS molecular weights being larger than those obtained using polystyrene standards, the molecular weights decrease with decreasing sizes of the side chains.

TABLE 3. Poly(3-alkylthiophene) Copolymers GPC Molecular Weight
Determination (Polystyrene Standards vs. Absolute)

Sample R-R'	RI Detector	UV Detector (254nm)	Multiangle Laser Light Scattering Detector (MALLS)		
	M_w	M_w	M_n	M_w	M_w/M_n
Hexyl-Octyl	114,000	134,000	159,000	442,000	2.8
Butyl-Octyl	129,000	119,500	60,300	128,000	2.3
Methyl-Hexyl	8,400	7,800	13,200	32,300	2.4
Methyl-Butyl	3,200	3,100	11,200	17,200	1.5

Smooth, free-standing, films of poly(3-decylthiophene) were cast onto glass plates from a trichloroethylene solution and oxidative doping with either $FeCl_3$ or $Fe(ClO_4)_3$ in acetonitrile led to conductivity increases as shown in Figure 1. Maximum conductivities of 5 Ω^{-1} cm^{-1} using $FeCl_3$
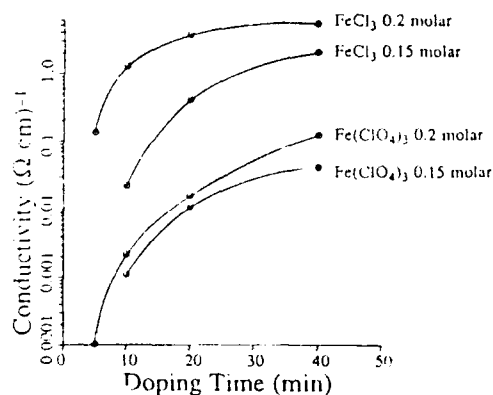

Figure 1. Conductivity of poly(3-decylthiophene) (4) films vs. doping time

and $.0^{-1}$ Ω^{-1} cm^{-1} for $Fe(ClO_4)_3$ were obtained. Dopant levels were obtained by weight uptake and, assuming $FeCl_4^-$ and ClO_4^- dopant ions respectively, result in compositions of $\{[C_4H(C_{10}H_{21})S]$ $[FeCl_4]_{0.19}\}_x$ and $\{[C_4H(C_{10}H_{21})S]$ $[ClO_4]_{0.02}\}_x$ for the most highly conducting samples. The lower conductivity observed for the $Fe(ClO_4)_3$ sample can most likely be attributed to a lower reactivity of this oxidant with the polymer leading to a lower dopant concentration. After doping and storing in air the conductivity of the sample is quite stable. In fact, some samples increased their conductivity slightly in air.

Solution pulled fibers were prepared and electron microscopy showed them to be space filling with surface pitting due to solvent evaporation. Further, polarized light optical microscopy indicated the fibers were birefringent with considerable orientation along the fiber axis.

Melt-spinning was next investigated as a means of processing poly(3-alkylthiophenes). Using a spinning speed of 5 m/min a significant quantity of poly(3-decylthiophene) fibers of 210 μm diameter were obtained which were quite flexible. The thermal stability of these melt-spun fibers, determined by TGA, was comparable to the virgin poly(3-decylthiophene). Both samples, under a nitrogen atmosphere, showed no weight loss to 200 °C, a gradual loss of about 10% to 420 °C followed by precipitous degradation.

As discussed earlier, the as made poly(3-alkylthiophenes) were very soluble in chlorinated solvents and dissolved quite rapidly. After processing, however, the fibers dissolved much more slowly and first underwent significant swelling. No cross-links were present, however, since the material ultimately dissolved completely. ^{13}C-NMR spectroscopy showed no change in the polymer structure. Films cast from solution had densities of 0.8 g/mL while, after melt processing, the fibers exhibited a density of 1.0 g/mL.

Doping studies with $FeCl_3$/CH_3CN provided maximum conductivities of 4 Ω^{-1} cm^{-1} after fairly short doping times of 10 minutes followed by a decrease in conductivity with longer doping times. One possibility here is that the fibers had become overoxidized at the longer times, a phenomenon seen in electrochemical studies.[13] There was no significant conductivity difference after melt spinning compared with before spinning.

An important consideration in solution doping studies is the possibility of inhomogeneous dopant ion distribution. In the case of a fiber this could lead to a highly conductive sheath surrounding an insulating core. A highly conducting, $FeCl_3$ doped, fiber was fractured under liquid nitrogen and investigated by electron microscopy and EDAX element mapping of both Fe and Cl. The distribution of both atoms indicated the fiber was homogeneously doped throughout its cross section. This was true even at rather short doping times. This indicates that the solvent and $FeCl_3$ are able to penetrate the polymer matrix quite rapidly and dope the polymer uniformly.

In order to improve the spinability several blends were prepared by melt-mixing 20% and 40% poly(3-decylthiophene) with 80 and 60% low density polyethylene. These were molded into rods (2.5 in. x 0.5 in.) and melt-spun into fibers. Spinning was much easier, with spinning speeds up to 58 m/min being readily achieved. Electron microscopy showed that these fibers were phase separated into large domains, with filaments of poly(3-decylthiophene) along the fiber axis. The original blend (before spinning) was also somewhat phase separated although the particles of poly(3-decylthiophene) were much more randomly oriented within the polyethylene. EDAX studies showed that the filaments were poly(3-decylthiophene) and the matrix was polyethylene. Attempted doping of these fibers demonstrated that they were non-conducting.

Preparation of a more homogeneous blend was achieved by codissolving 60% poly(3-decylthiophene) and 40% polyethylene in hot xylene and removing the xylene by distillation. Electron micrographs of this blend showed that it was quite homogeneous, with little observable phase separation. Upon melt forming the rod (for the melt-spinning) there was an apparent modest increase in the phase separation with the majority of the material appearing uniform. Melt-spinning of this rod produced a fiber which now appeared quite homogeneous. Polarized optical transmission microscopy showed that the fibers were birefringent with considerable orientation along the fiber axis. Doping with I_2 gave a conductivities of about $10^{-1} - 1\ \Omega^{-1}\ cm^{-1}$. It should also be mentioned that these fibers were still more readily spinnable, with spinning speeds up to 151 m/min having been used.

A previous study of melt spun fibers (25 μm diameter) of poly(3-dodecylthiophene)[8] also gave flexible fibers, which were reported to have conductivities of up to 55 $\Omega^{-1}\ cm^{-1}$ when doped with iodine. No other properties of the fibers were reported.

ACKNOWLEDGEMENTS

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